Atmospheric P deposition to the subtropical North Atlantic: sources, properties, and relationship to N deposition

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[1] Biogeochemical studies show that the surface waters of the subtropical North Atlantic are highly phosphorus (P) stressed. Human activity may exacerbate phosphorus stress by enhancing atmospheric nitrogen (N) deposition and raising N/P ratios in deposition. However, the magnitude of this effect is unclear, in part, because atmospherically deposited phosphorus sources are not well known, particularly the contribution from organic phosphorus. Here we report measurements of phosphorus in aerosols and wet deposition at Miami and Barbados. African dust is the major aerosol P source at both Miami and Barbados, containing ~880 ppm total phosphorus and ~70 ppm soluble reactive phosphorus (SRP). Organic compounds contribute, on average, 28%–44% of soluble phosphorus in precipitation. Because of dust transport seasonality, phosphorus inputs to the North Atlantic are expected to be highly variable with 2–10 times more P deposition during summer than winter. Pollution is also an important contributor to total and soluble phosphorus in Miami aerosols and deposition. Estimated SRP deposition in Barbados and Miami is 0.21 and 0.13 $\mu mol\, m^{-2}\, d^{-1}$ phosphorus, respectively. Inorganic nitrogen in excess of Redfield ratio expectations in deposition was very different between the sites, totaling 21–30 and 127–132 $\mu mol\, m^{-2}\, d^{-1}$ nitrogen in Barbados and Miami, respectively; the high deposition rates at Miami are linked to pollutants. Including soluble organic nitrogen and phosphorus halved the estimates of excess nitrogen in Barbados wet deposition. Thus, the organic phosphorus fraction is important in the assessment of the magnitude of biogeochemical change of the North Atlantic caused by atmospheric deposition.

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1. Introduction

[2] Atmospheric phosphorus (P) is the dominant source of new, nonrecycled, P to surface waters of the open ocean. Therefore, even though it is a relatively small source of P compared to other sources [*Okin et al*., 2011], atmospheric P can have a large impact on long-term nutrient limitation patterns if its relationship to new, nonrecycled, nitrogen (N) changes as it is currently doing. Over the past 150 years, the deposition of N compounds is estimated to have doubled [*Duce et al*., 2008], while the deposition of P species has remained relatively steady [*Baker et al*., 2003; *Mahowald et al*., 2008]. Consequently, recent modeling studies predict an atmospheric deposition-driven increase in P depletion in surface waters of some ocean regions relative to preindustrial times [*Kanakidou et al*., 2012; *Kim et al*., 2011; *Krishnamurthy et al*., 2007, 2009; *Zamora et al*., 2010]. However, the atmospheric fluxes of P to the ocean are poorly characterized compared to N deposition fluxes. Thus, our ability to assess the impact of atmospheric deposition on surface nutrients is limited by our understanding of atmospheric P deposition.

[3] A better knowledge of atmospheric P inputs is of particular interest in the subtropical North Atlantic region, which is already P stressed (as defined by observed physiological responses of local organisms to low phosphate concentrations [*Lomas et al*., 2010]). In this region, surface phosphate levels are extremely low, with concentrations sometimes reaching subnanomolar levels [*Wu et al*., 2000]. Regional P stress is evident in the high activity of alkaline phosphatase in surface gyre waters [*Lomas et al*., 2004], high turnover rates of phosphate [*Sohm and Capone*, 2010], and the adaptive ability of some organisms to substitute non–P-containing lipids for phospholipids in cell walls [*Van Mooy et al*., 2009]. Selective removal of P from dissolved organic matter [*Clark et al*., 1998] and high N/P ratios of nutrients in the main thermocline [*Ammerman et al*., 2003; *Fanning*, 1992] are also observed. In some organisms, particularly diazotrophs, P is even thought to

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be limiting or colimiting growth [*Mills et al*., 2004; *Moore et al*., 2008; *Sañudo-Wilhelmy et al*., 2004].

[4] Despite the potential impact of atmospheric P on nutrient limitation, many questions remain regarding its magnitude, sources, solubility, and bioavailability. Mineral dust is the primary source of soluble atmospheric P in the North Atlantic subtropical gyre region [*Mahowald et al*., 2008]. However, other sources of atmospheric P have been observed, as well, including biomass burning and anthropogenic combustion processes [*Allen and Miguel*, 1995; *Artaxo et al*., 2002; *Baker et al*., 2006a; *Chen and Chen*, 2008; *Gaudichet et al*., 1995; *Mahowald et al*., 2005; *Ternon et al*., 2011; *Tsukuda et al*., 2006; *Zhang et al*., 2002], primary biogenic particles [*Graham et al*., 2003; *Mahowald et al*., 2005], and sea spray [*Chen et al*., 1985; *Graham et al*., 1979]. *Mahowald et al*. [2008] suggested that because anthropogenic P tends to be more soluble, it may have a larger impact on open-ocean processes relative to other P sources.

[5] In order to understand how atmospheric P deposition affects surface water nutrient dynamics, both its deposition rates and its bioavailability must be resolved. *Anderson et al*. [2010] found that only 15%–30% of P was likely to be bioavailable in dust-dominated samples from the Gulf of Aqaba. However, the majority of previous studies have focused on total phosphorus (TP) in deposition. At minimum, the soluble reactive phosphorus (SRP) fraction of TP is available to organisms, but measured SRP values vary greatly, ranging between 7% and 100% of TP (*Mahowald et al*. [2008, and references therein]). Consequently, it is difficult to predict the SRP fraction despite some observed trends in P solubility as a function of aerosol source [e.g., *Herut et al*., 1999; *Nenes et al*., 2011].

[6] Atmospheric organic phosphorus is also of interest because it is likely to be at least partially bioavailable (based on the specialized ability of organisms in the subtropical North Atlantic to break organic P bonds) [*Lomas et al*., 2010]. One study indicated that organic phosphorus could contribute up to 94% of the total soluble P (TSP) [*Chen et al*., 1985]. Unfortunately, very few studies have measured the dissolved organic P (DOP) fraction in atmospheric deposition [e.g., *Chen et al*., 1985, 2006, 2007; *Graham et al*., 1979; *Markaki et al*., 2010; *Migon and Sandroni*, 1999; *Rolff et al*., 2008; *Williams et al*., 1997], and these indicate that the contribution of DOP to TSP is widely variable (ranging from 22% to 94% of TSP). Additionally, the contribution of recycled marine DOP may be quite high [*Kanakidou et al*., 2012]. Consequently, it is difficult to quantify the importance of organic P.

[7] Here we present the results of measurements of P in aerosols and precipitation made in studies at two sites in the western subtropical North Atlantic—Miami and Barbados. We report both soluble organic P measurements from rain and also report on measurements of aerosol P determined from a unique time series of aerosol samples gathered over two decades (1989–2008) at these sites. We selected samples that were collected under conditions where we would expect a specific source type would be dominant (e.g., biomass burning, dust, pollution) so that we could better characterize end-member source characteristics. We then evaluate the effect of aerosol source on the solubility and magnitude of P deposition to the North Atlantic subtropics, particularly in the context of the amount of potential N stress from atmospheric deposition that could be alleviated by P deposition.

2. Methods

2.1. Environmental setting

[8] Atmospheric P was sampled at Miami, Florida, USA (25°N, 83°W) and Barbados, West Indies (13°N, 59°W), both located in the western subtropical North Atlantic. The sampling sites and protocols have been previously described in detail, and so they are only summarized here [see *Trapp et al*., 2010b, *Zamora et al*., 2011 for further discussion]. Samples in Barbados were collected from a 17-m-high tower 30-m above sea level on the edge of a cliff on the easternmost (windward) side of the island. Miami samples were gathered from a rooftop on Virginia Key (~20-m above ground/sea level). Aerosol sampling is computer controlled to activate only during easterly onshore winds (between 335° through North to 130° in Barbados and 45°–204° in Miami) to avoid local contamination. On specific occasions, discussed below, sector control is deactivated in order to sample winds from all directions so as to assess the impact from pollution sources.

[9] For both sites, mineral dust is the primary source of aerosols during the summer [*Li et al*., 1996; *Prospero and Lamb*, 2003; *Prospero*, 1999]. Barbados receives about 2.5 times more dust annually than Miami owing to higher dust concentrations and a longer dust transport season [*Prospero*, 1999]. However, the multiday time scale (n) of dust episodes and aerosol distributions gathered from remote sensors indicate that dust aerosol composition is similar in both Miami and Barbados [*Trapp et al*., 2010a], as well as the rest of the western subtropical region [*Prospero*, 1999]. Sea spray is another common aerosol source in both sites. Sea salt aerosol concentrations are lower at Miami than at Barbados because of weaker winds and the presence of the Bahamas to the east that acts to suppress large seas. Both sites can be impacted by biomass burning aerosols. In Miami, biomass burning events are common in the spring because of fires in the Everglades, the eastern boundary of which is 30 km from our site. The Miami site also receives aged biomass burning aerosols transported from mid-Atlantic North America over the North Atlantic and then retroflected back to the coast [*Zamora et al*., 2011]. Barbados receives smoke transported long distances from sub-Saharan Africa and possibly South America [*Zamora et al*., 2011]. On Barbados, local pollution does not impact on our samples because of sampling controls (see section 2.2) and the location of our site on the extreme eastern coast of the island. In contrast, in Miami local and regional pollution can impact our samples all year round because of land-sea breeze effects. Pollution aerosols are particularly common during the winter when wind patterns periodically shift in conjunction with cold-front passages so that Miami receives northerly air masses [*Prospero*, 1999; *Prospero et al*., 2010].

2.2. Sample collection

[10] Rain was sampled on an event basis (Table 1) using automatic samplers. A polyethylene bucket was initially used to capture rain, but starting in April 2008, a stainless steel bucket was used for N, P, and C measurements instead in an effort to reduce carbon blanks. The change in bucket type did not affect P blank concentrations. Trace metals continued to be gathered in a parallel secondary collector fitted with the polyethylene bucket. Precipitation samples were

Table 1. Sampling Site Characteristics, Sampling Dates, and Sample Numbers

Characteristics of sampling sites, periods of record, and numbers of samples						
Site	Latitude	Longitude	Annual precipitation[a] ($cm\,yr^{-1}$)	Sample type	Period of record	No. of samples
Miami	13°N	59°W	133.2	Rain	Mar 2007–Dec 2008; Apr-Aug 2009	137
				Aerosols (bulk)	Jan 2007–Aug 2008	52
				Aerosols (size segregated)	May-July 2008; Oct-Nov 2008, periodically	28
Barbados	25°N	83°W	76.7	Rain	Aug-Sept 2007; Aug-Sept 2008	22
				Aerosols (bulk)	July 1988–Sept 2008	33
				Aerosols (size segregated)	Aug-Sept 2008	8

[a]Average annual rainfall from M. D. Winsburg, Precipitation data: Miami, 2009, Florida Climate Center, http://coaps.fsu. edu/climate_center/data/precip_miami.shtml and *Rouse* [1962].

gathered as soon as practical (and always within 24 h) post–rain event and were then filtered immediately (0.2-μm Supor® polyethersulfone filters for all analytes except trace metals, which were filtered with a 0.45-μm polytetrafluoroethylene filter). Samples were then frozen until analysis.

[11] High-volume, 24-h bulk aerosol samples were collected on Whatman-41 cellulose filters (nominal flow rate $\sim 0.014\,m^3\,s^{-1}$) using wind sector controls, except as noted. Upon collection, these samples were folded, sealed in Ziploc bags, and frozen immediately in the dark at $\sim -15\,°C$ in order to reduce the potential for chemical reactions on the filter during storage. These samples were primarily collected in 2007 and 2008. We also collected and analyzed size-segregated samples using a high-volume Sierra brand cascade impactor (flow rate $\sim 0.018\,m^3\,s^{-1}$), following the procedure of *Zamora et al*. [2011], with samples being collected nominally every 3–4 days to increase likelihood of obtaining detectable concentrations. In addition, we utilized historic filter data that had previously been collected in ongoing long-term studies using data beginning in 1973 in Barbados and 1998 in Miami where samples were collected nearly every day. Upon collection, these earlier samples were also sealed in Ziploc bags, but they were stored at room temperature. We gathered field and lab blanks for all filters and subtracted them from the sample values as discussed later.

2.3. Sample and data analysis

[12] Various protocols have been used to characterize water-soluble P in aerosols using a variety of aqueous solutions or seawater as the extraction media. *Chen et al*. [2006] extracted aerosol samples in pure water for 30 min with sonication and obtained slightly higher SRP yields than with samples extracted in low-nutrient seawater (LNSW). *Ridame and Guieu* [2002] also observed greater SPR yields in pure water than in LNSW for gently stirred solutions containing Saharan soil particles. However, *Nehring* [1976] found that although the extraction rate of P from Saharan dust was slower in seawater than in pure water, the amount of extractable P was similar when longer extraction times were used. *Aminot and Andrieux* [1996] observed that it took longer for P in soil samples extracted in LNSW to attain the same levels as samples extracted in buffered deionized water, but they determined that similar levels of SRP were eventually released from the soil samples as long as the pure water samples were buffered (as P desorption from particles can be pH sensitive). It is unclear whether *Chen et al*. [2006] would have obtained different results if they had employed a longer extraction time. Also, neither *Chen et al*. [2006] nor *Ridame and Guieu* [2002] used buffered pure water for their extractions.

[13] In our procedure, we used deionized water ($\Omega > 18.0$) that had been buffered with 2.5 mmol $NaHCO_3$ to a pH of ~8 to extract aerosol filters in order to approximate seawater pH [*Aminot and Andrieux*, 1996] because we believed that it was essential to control the pH of the extracting solution. For clarity, note that rain samples were not buffered. Aerosol filter portions were then immersed in 45 mL of extractant solution, vigorously shaken, and stored in the dark for 12 h to allow desorption (preliminary tests indicated that full desorption had been reached at ~10 h). We then filtered the aerosol extracts through a 0.2-μm Supor® filter.

[14] Upon filtration, rain and aerosol samples were either immediately analyzed or stored frozen until analysis. P was analyzed colorimetrically using a 2-m liquid waveguide capillary cell using the procedures described in *Zhang and Chi* [2002] and *Zhang et al*. [1999]. Because this procedure can hydrolyze some reactive organic P compounds in addition to orthophosphate [*Benitez-Nelson*, 2000], the P determined in this procedure is referred to SRP instead of dissolved inorganic P. Total soluble phosphorus (TSP) in rain was analyzed by adding 30 mmol H_2O_2 and UV oxidizing the samples for 2 h with a 1425-W Hg lamp and then analyzing the samples colorimetrically similarly to SRP. Rain DOP was calculated as the difference between TSP and SRP.

[15] *Vaz et al*. [1992] observed that Al in soil samples may be liberated during the UV oxidation step, causing a loss in observed TSP because of adsorption of PO_4^{3-} onto aluminum hydroxides. Because our samples included dust particles, we tested whether this process would impact our TSP recovery. Several of the most dusty aerosol subsamples were run with and without the addition of F^-, which acts to preferentially bind aluminum hydroxides [*Vaz et al*., 1992]. No reduction in TSP was found ($p > 0.05$, paired t test), and consequently, we omitted this step in the analysis of the remainder of the samples.

[16] TP in aerosols was determined by the addition of a $MgSO_4$ solution to a filter subsample followed by combustion at 500 °C and dissolution with 7.5 m*M* HCl (similar to *Solorzano and Sharp* [1980]). Dust mass was determined by extracting water-soluble species from the Whatman 41 filter and then ashing the filter at 500 °C; the residue is attributed to dust [*Savoie et al*., 2002]. Non–sea-salt sulfate ($nss\text{-}SO_4^{2-}$), NO_3^- (in samples collected prior to 2007), and Cl^-, Na^+, K^+ ions were determined by suppressed ion chromatography and flame atomic absorption spectrophotometry [*Savoie et al*., 2002]. Trace metals in rain, including Fe, V,

Ti, Mn, and As, were determined using inductively coupled plasma mass spectroscopy, using the methods described by Trapp [2009]; trace metal blanks were always below instrumental dection limits. Detection limits and blank values for N and P are listed in Table 2. Aerosol detection limits were determined as 3 times the standard deviation of the blank multiplied by an air volume of 1000 m^3; rain detection limits were determined as 3 times the standard deviation of the blank.

[17] Some samples had DOP concentrations below the DOP method detection limit (MDL) of 8 n*M* (Table 2), which introduced additional analytical uncertainty. To avoid introducing biasing the data toward higher values by systematically removing low values, we include all DOP values, even those below the MDL (similarly to *Keene et al*. [2002]). Organic P in aerosol samples was not measured because of high-filter blanks.

[18] Although atmospheric P is the major focus of this paper, we later examine the P results in terms of the impact on N/P ratios in seawater and nutrient stress. The N data that we use were obtained in concurrently collected samples at Miami and Barbados. For samples more recent than 2007, the techniques used and results are presented in *Zamora et al*. [2011] (in brief, WSIN was determined spectrophotometrically, total soluble nitrogen (TSN) was determined with a Shimadzu TOC-V total carbon analyzer combined with a TNM-1 total N analyzer, and WSON was operationally defined as the difference between the two). For older samples that had already been analyzed, analytical procedures are detailed in *Savoie et al*. [2002] (in brief, only inorganic N was determined: NO_3^- via ion chromatography and NH_4^+ via spectrophotography).

2.4. Sample selection and determination of aerosol sources

[19] Given the very large number of aerosol samples (n 1.5×10^4), only a portion of the bulk aerosol data set was selected for analysis. We mainly focused on samples from 2007 and 2008 to avoid the risk of longer-term storage issues regarding SRP analysis. Because our primary objective was to understand the P contribution from various sources, we selected samples (as described later) that were primarily dominated by a specific type of aerosol source (i.e., dust, pollution, etc.). All samples from the Barbados field campaigns in summer 2007 and summer 2008 were analyzed.

[20] We determined which samples were predominantly influenced by a given aerosol source type (e.g. dust, biomass burning, sea spray, and pollution) using the procedure described in *Zamora et al*. [2011]. In short, we primarily based our aerosol source classifications on the chemical properties of the aerosols including the concentrations and ratios of dust, sea salt, non–sea-salt noncrustal K^+ [*Andreae*, 1983] (a biomass burning indicator), and non–sea-salt SO_4^{2-}. To further interpret our data, we used filter coloration and ground-based lidar data (available in Barbados only) and satellite data (from the Moderate Resolution Imaging Spectroradiometer [MODIS], the Geostationary Operational Environmental Satellite [GOES], and the Sea-viewing Wide Field-of-view Sensor [SeaWiFS]). We identified Saharan air masses with the presence of the Saharan Air Layer (SAL; *Carlson and Prospero* [1972]) using vertical profiles of wind direction and water vapor (data from routine weather service measurements made in Miami and Barbados). Samples with characteristics associated with more than one aerosol source (e.g., dust mixed with pollution) were labeled as having a mixed source. Source determination of rain samples was based on the source determination of the aerosols from that day. For further detail on source determination criteria, see *Zamora et al*. [2011]. Finally, we computed 10-day HYSPLIT back trajectories (R. Draxler and G. D. Rolph, HYSPLIT [HYbrid Single-Particle Lagrangian Integrated Trajectory] Model access via NOAA ARL READY Web site, 2011, http://ready.arl.noaa.gov/HYSPLIT.php), which were partitioned according to aerosol type, as in *Zamora et al*. [2011].

[21] Note that by classifying an air mass as a given source type, we do not mean to imply that we are sampling the pure end-member aerosol source (e.g. a sample classified as "dust" may not be completely representative of the original dust aerosol source and may include aerosols from other source types such as pollution and biomass burning). Instead, the source classification scheme attempts to identify which aerosol source type has had the largest influence on that sample. These source classifications are then used to draw conclusions about trends in end-members.

3. Results and Discussion

3.1. Aerosol phosphorus

3.1.1. Total phosphorus

[22] There is a close relationship between dust concentrations and TP concentrations in aerosols at Barbados and Miami (Figure 1). Dust is clearly the primary source of TP to both sites (and, presumably, to the western and tropical North Atlantic). Within these results (Figure 1b), samples were further classified as dominated by "pollution," dust, "sea spray," and "biomass burning" (see section 2.4). In Barbados, TP concentrations were highly correlated with dust (Figure 1a); in Miami, the TP concentrations in most samples were also highly correlated with dust (Figure 1a), but there were notable exceptions that yielded high TP values at low dust concentrations. In Figure 1b, those samples classified as dust show a high correlation of TP with dust. However pollution samples frequently have higher

Table 2. Aerosol and Wet Deposition Filter Blank Values and Detection Limits

	Filter blanks (nmol $filter^{-1}$) ($n = 13$)	Filter detection limits (nmol m^{-3})	Rain blanks (μ*M*) ($n = 15$)	Rain detection limits (μ*M*)
SRP	11 ± 10	0.030	0.006 ± 0.009	0.028
DOP	n.a.	n.a.	0.001 ± 0.009	0.028
TP	47 ± 22	0.065	n.a.	n.a.
NO_3^-	0.1 ± 0.2	0.5	0.2 ± 0.2	0.7
NH_4^+	2.9 ± 1.0	3.1	0.1 ± 0.4	1.1
WSON	0.0 ± 0.2	0.9	0.0 ± 0.4	1.1

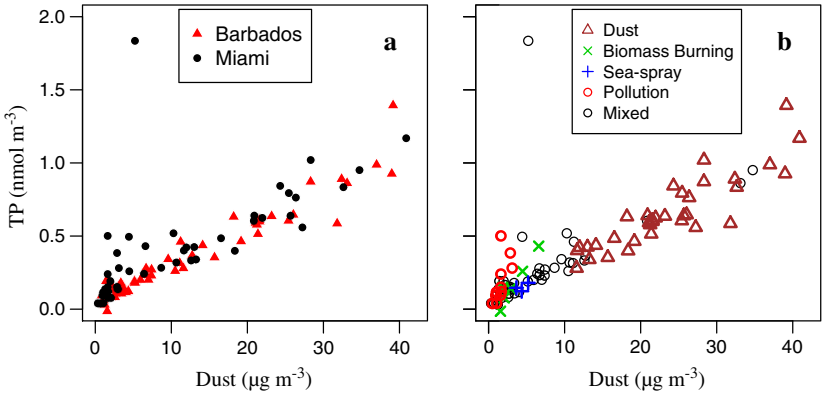

Figure 1. Aerosol TP concentrations as measured in all bulk aerosol samples from Barbados and Miami: as a function of (a) dust concentrations and (b) sample source classification.

concentrations of TP than would be expected based on dust concentrations alone. In Barbados, no such deviations were observed, which is consistent with the fact that there were no days during which pollution was clearly the dominant source of aerosols. We conclude that pollution was a secondary but more minor source of TP in Miami and a nearly negligible source of TP in Barbados.

[23] The correlation between dust and TP has been observed by others using Al as a proxy for dust [*Anderson et al*., 2010; *Bergametti et al*., 1992; *Graham and Duce*, 1982; *Migon and Sandroni*, 1999; *Özsoy*, 2003; *Tsukuda et al*., 2006]. However, in Miami and Barbados, the relationship between TP and dust is particularly clear. The high correlation could be caused by a number of factors. First of all, previous studies have shown that the composition of dust collected at Miami and Barbados is relatively homogeneous [*Trapp et al*., 2010a]. The impact of P-containing pollution is relatively low at the Miami and Barbados sites compared to other global sites reported in the literature (e.g., *Ternon et al*. [2011]). In addition, in our protocol we actually measure dust concentrations instead of using the concentration of some element, typically Al, as a proxy for dust. Also, data variability is reduced because we were able to select days most likely to be dominated by single-source types. Finally, Miami and Barbados are not strongly affected by biomass burning during the summer when most of the samples were taken. In some other regions, such as sub-Saharan Africa, the relationship between dust and TP may be masked by high levels of biomass burning and lower levels of dust [*Baker et al*., 2006b; *Losno et al*., 1992]. The biomass burning samples at our sites provided much less TP (169 ± 142 pmol m^{-3}) than the dust days (651 ± 249 pmol m^{-3}). Because of the relatively high frequency of dust events over the Tropical Atlantic, we conclude that TP input from biomass burning in the western subtropical North Atlantic is likely to be much smaller than TP input by dust.

[24] The correlation between TP and dust in dust-only samples from Miami and Barbados is shown in Figure 2. On the basis of the slope of the relationship, the elemental concentration of TP in African dust aerosols was ~880 ppm. This value falls close to the interquartile range of values previously observed for aeolian dust (640–870) and the fine fractions of Saharan soil (540–950) [*Guieu et al*., 2002].

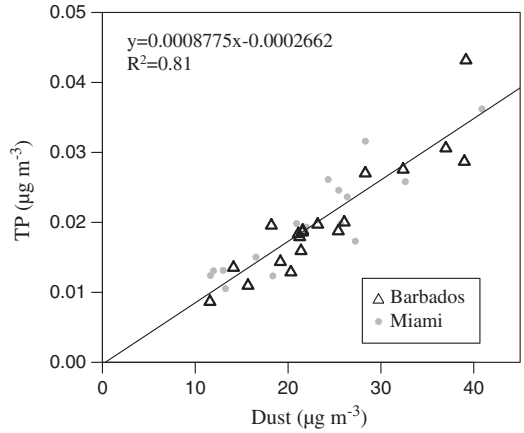

Figure 2. The relationship between total phosphorus and dust in Barbados (black triangles) and Miami (gray circular dots) on dust days. The slope of the regression line for data from all dust days at both sites combined yields a TP concentration of ~880 ppm in dust aerosols.

Table 3. SRP Concentrations (pmol P m^{-3}) in Size-Segregated Aerosols Sampled Periodically Between 7 August to 6 September 2008 in Barbados and 13 May to 19 November 2008 in Miami[a]

		SRP (pmol m^{-3})		
	n	Fine	Coarse	%Fine
Barbados				
Dust	3	18 ± 20	34 ± 9	33 ± 31
All data	7	22 ± 14	27 ± 10	44 ± 21
Miami				
Dust	6	105 ± 65	55 ± 22	63 ± 12
Biomass burning	7	61 ± 49	21 ± 14	70 ± 12
Pollution	3	13 ± 3	18 ± 28	65 ± 41
All data	29	47 ± 53	25 ± 24	67 ± 20

[a]The cutoff between fine and coarse aerosols was 1 µm in Barbados and either 0.5 µm (n = 14) or 1 µm (n = 15) in Miami.

3.1.2. SRP and solubility

[25] Here we present size-segregated and bulk SRP data. As shown in Table 3, about half of SRP particles are present in the submicron size fraction, similar to observed North Atlantic samples, where 55% of SRP was present in the

submicron fraction (from *Mahowald et al.* [2008], supplementary materials).

[26] While TP transport to the western subtropical North Atlantic appears to be nearly entirely dust derived, bulk aerosol data indicate that the sources of SRP are more complex (Figure 3), with comparable contributions from dust, sea spray, pollution, and biomass burning (Figure 3; Table 4). Thus, although SRP at each site has a positive relationship with dust (Figure 3, $r^2 = 0.19$), the relationship is not as strong as it is with TP ($r^2 = 0.81$). When dust days are subsampled, the relationship between SRP and dust is clearer (Figure 4), at least in Barbados. dust samples in Barbados contain ~70 ppm SRP (based on the slope).

[27] In comparison, the relationship between dust and SRP within Miami dust samples has a higher slope (150 ppm) and is more variable (Figure 4b). Also, size-segregated Miami aerosols have a greater relative percent of submicron SRP than Barbados (67% versus 44%, respectively) and an average of 87 pmol m^{-3} more fine SRP in dust samples than in Barbados (Table 3).

[28] Some dust samples in Miami have greater SRP than would be expected based on the dust-SRP relationship in Barbados (Figure 4), which is likely due either to the addition of pollution-derived SRP or greater solubility of dust P in the presence of pollution-derived acidity [*Nenes et al.*, 2011]. Pollution also is the likely cause for the greater relative percentage of SRP in the submicron fraction as pollution is the dominant source of P in the submicron size fraction at other locations [*Vicars and Sickman*, 2011], and it is pervasive in Miami even on days dominated by dust [*Trapp et al.*, 2010a; *Zamora et al.*, 2011]. Additionally, while studies from other locations indicate that SRP is related to dust (e.g., *Baker et al.* [2006a]), they also show that pollution and biomass burning sources of SRP can have a large effect on total SRP concentrations (e.g., *Baker et al.* [2010]; *Furutani et al.* [2010]). Interestingly however, there are multiple points below the Barbados dust-SRP line (the red line shown in Figure 4b). It is unclear why SRP values in some Miami dust samples should fall below the range of data in the dust-SRP correlation from Barbados; speculatively, perhaps unknown interactions with pollution may cause this effect.

[29] One reason why pollution and biomass burning samples generally have more aerosol SRP than would be expected based on their contribution to TP (Figures 1 and 3) is because they are nearly twice as soluble as dust samples (Table 4). Previous studies in a variety of other locations similarly report higher P solubility in combustion-derived aerosols than in dust (e.g., *Bergametti et al.* [1992], *Graham and Duce* [1982], *Herut et al.* [1999], *Baker et al.* [2006b]). Although it is possible that marine sea spray particles mixed in with the pollution samples enhanced the apparent

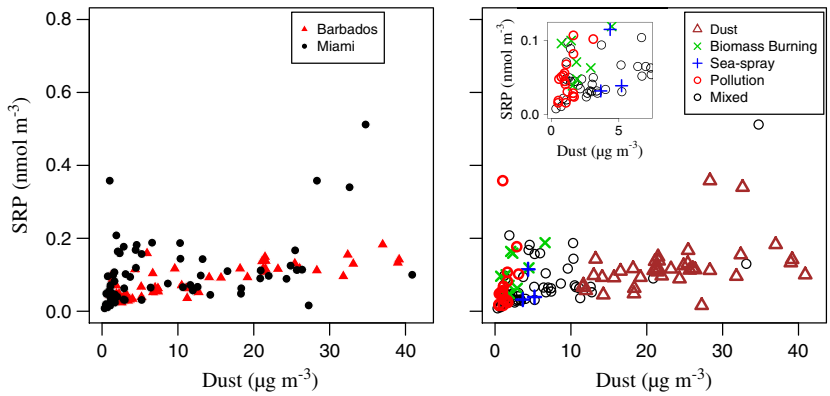

Figure 3. Aerosol SRP concentrations: (a) as a function of dust concentrations in Miami and Barbados and (b) according to sample source classification. The inset in the right-hand panel shows the data at low concentrations.

Table 4. Aerosol TP and SRP Concentrations and Solubility in Miami and Barbados According to Sample Sources (%SRP/TP Is Only Estimated for Samples With SRP Concentrations Greater Than Filter Detection Limits of 78 pmol P m^{-3})[a]

	TP (pmol P m^{-3})			SRP (pmol P m^{-3})			SRP/TP (%)	
	n	av. ± s.d.	Median	*n*	av. ± s.d.	Median	*n*	Median
Barbados								
Dust	19	654 ± 263	605	20	121 ± 27	117	17	19
Sea spray	4	110 ± 83	135	3	62 ± 46	39	1	94
Biomass burning	3	91 ± 91	139	3	53 ± 17	48	0	b.d.
All data	54	380 ± 312	275	53	85 ± 43	89	24	21
Miami								
Dust	16	647 ± 241	632	19	119 ± 89	100	12	19
Biomass burning	4	227 ± 155	200	7	127 ± 45	119	2	45
Pollution	13	182 ± 142	120	19	71 ± 80	48	4	35
All data	55	380 ± 346	283	70	99 ± 90	72	23	23

[a]An abbreviation of "b.d." indicates that all samples were below detection limits.

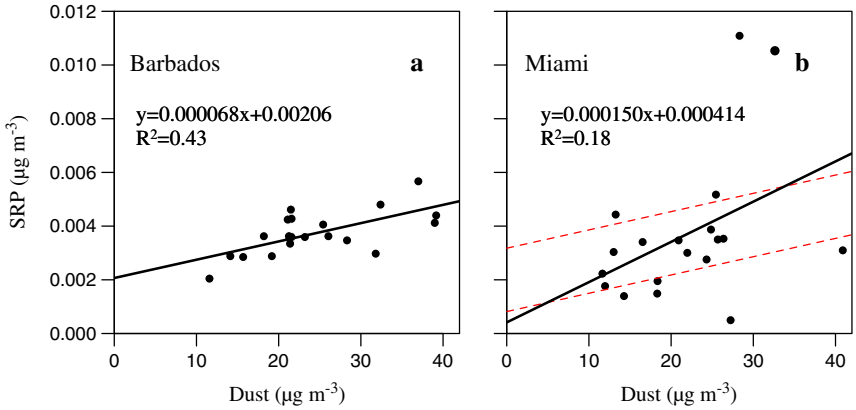

Figure 4. The concentration of SRP in mineral dust based on samples collected on dust days. The slope of the black regression line yields a P concentration of (a) ~70 ppm in Barbados and (b) ~150 ppm in Miami (minus outliers at the top, ~30 ppm). The greater scatter of the data from the Miami samples relative to Barbados samples is most likely caused by the presence of pollution aerosols in Miami even on days dominated by dust. For comparison, the red dashed lines in Figure 4b show the regression slope and range of the Barbados data shown in Figure 4a.

solubility, samples where this effect would be greatest were excluded from the analysis (i.e. samples with a sea salt: nss-SO_4^{2-} ratio of >0.9 μg/nmol).

[30] In comparison to the subtropical North Atlantic sites in this study, *Herut et al*. [1999] observed in the Mediterranean ~260 ppm of seawater leachable inorganic P from dust aerosols. The higher SRP concentrations observed by *Herut et al*. [1999] may be caused by the different dust sources that impact the Mediterranean, but admixing of pollution from Europe is also likely to be a major factor either by the addition of pollutant P or by the enhanced solubility of P through the effects of acid pollution species [*Nenes et al*., 2011; *Srinivas and Sarin*, 2012].

[31] There is a high *y*-intercept of ~209 pg SRP m^{-3} in Figure 4a, which indicates that there is an additional SRP source other than dust in Barbados on the dust days sampled. Because Barbados is a relatively pristine marine site, it is unlikely that this source of extra SRP is from pollution. Interestingly, if the two outliers shown in the top right of Figure 4b are excluded (these were the two samples with the highest nss-SO_4^{2-} concentrations and presumably highest pollution levels), the *y*-intercept for the Miami dust-SRP relationship becomes similar to that in Barbados (~225 pg m^{-3} as compared to 209 pg m^{-3}).

[32] Because the consistency of the offset in Barbados, we hypothesize that this extra SRP is caused by sea spray and not some other source, such as biomass burning. In support of this hypothesis, the intercept value in Figure 4a is equivalent to 67 pmol m^{-3}, which is similar to the average sea spray sample concentration in Barbados (62 pmol m^{-3}, Table 4). The scatterplot for TP versus dust shown in Figure 1a for Barbados yields an intercept of 53 pmol m^{-3}, indicating that if sea spray is the reason for the additional P source, then it is primarily in the form of SRP. This agrees with the one sea-spray SRP/TP sample shown in Table 4. Additionally, the size distribution of SRP in Barbados dust samples (Table 3) indicates that there is a large contribution from fine aerosol particles. Sea spray production processes have previously been associated with the production of fine particles [*Andreae and Rosenfeld*, 2008], and sea spray has been suggested as a source of atmospheric P [*Graham et al*., 1979].

[33] This likely sea-salt SRP source in our samples appears to contribute about half of the aerosol SRP measured in Barbados during the collection months of August-September. As recycled oceanic P, sea spray–derived SRP does not contribute new P to the ocean. Therefore, it must be accounted for in order to not overestimate "new" atmospheric SRP deposition to the ocean from external sources. To do so, we isolate the dust-derived SRP from the slope of 70 ppm shown in Figure 4a, disregarding the offset and thus the contribution from what we believe to be sea spray. Miami samples were not used to calculate the SRP contribution from dust because of the impacts of pollution at that site.

[34] On the basis of the aerosol average of 880 ppm TP and 70 ppm SRP (Figures 3 and 4a), dust SRP is expected to contribute 8% (Barbados) to 18% (Miami) of aerosol P—which is slightly less than expected from the concentration-driven solubility indicated in Table 4 (~19%). This difference in average solubility at each site is likely caused by the impact of sea-salt SRP on the net concentration in Table 4. The 8%–18% solubility at our sites is relatively close to the globally estimated average of about 17% [*Mahowald et al*., 2008].

3.2. Phosphorus in rain

[35] Volume-weighted SRP and DOP concentrations in rain from Miami and Barbados, distinguished by different source types, are presented in Table 5. DOP formed a large portion of TSP in rain, contributing 28% of TSP in Barbados and 44% in Miami. DOP has also been observed in aerosols in relatively high proportions (contributing ~60% of TSP in the Tahoe Valley [*Zhang et al*., 2002] and 31% in the Mediterranean [*Chen et al*., 2007]). The greater contribution of DOP to TSP in Miami relative to Barbados may reflect, to some extent, the lower SRP inputs from dust in Miami as compared to Barbados because of the shorter dust transport season in Miami. In Barbados, SRP in dust-dominated rain samples typically contributed 76%–93% of TSP; the median DOP/TSP ratio was 7% compared to 24% in Miami

Table 5. Measured Volume-Weighted Mean N and P Concentrations in Rain at Miami and Barbados (±Volume-Weighted Standard Deviation, With Volume-Weighted Median Presented in Parentheses)[a]

	n	SRP (n*M*)	TSP (n*M*)	DOP (n*M*)	Median DOP/TSP (%)[b]	DIN (μ*M*)	DON (μ*M*)	Median DIN:SRP ratio[b]	Median TSN:TSP ratio[b]
Barbados									
Observed									
All Data	21	59.3 ± 36.6 (46.7)	76.9 ± 39.4 (64.4)	17.6 ± 10.5 (11.2)	28	7.1 ± 3.9 (5.1)	0.8 ± 1.1 (0.2)	172	113
Dust	6	110.4 ± 32.7 (105.2)	119.4 ± 32.2 (32.2)	8.9 ± 3.4 (8.5)	7	11.6 ± 5.4 (16.2)	0.8 ± 0.8 (1.2)	103	107
Biomass burning	1	23.6	33.7	10.0	30	3.3	−0.2	139	91
Sea spray	2	28.5 ± 18.2 (18.0)	49.4 ±35.8 (28.8)	21.3 ± 17.5 (11.2)	40	5.4 ± 0.4 (5.1)	2.3 ± 0.3 (2.5)	284	263
Estimated[c]									
All data	5351	45.1 ± 61.3 (21.7)	–	–	–	5.4 ± 9.0 (4.1)	–	161	–
Miami									
Observed									
All data	67	26.3 ± 24.9 (14.5)	65.5 ± 38.3 (42.7)	37.7 ± 22.6 (32.2)	44	17 ± 9.9 (11.4)	1.3 ± 1.6 (1.0)	474	246
Dust	3	90.5 ± 64.1 (45.8)	131.2 ± 64.4 (166.8)	22.9 ± 8.3 (20.7)	24	24.1 ± 12.5 (18.0)	2.0 ± 0.6 (2.3)	145	283
Biomass burning	3	152.6 ± 23.6 (150.7)	150.9 ±24.7 (155.0)	−1.7 ± 3.9 (−3.9)	0	67.9 ± 9.8 (77.0)	5.9 ± 1.2 (6.7)	420	468
Pollution	6	21.0 ± 8.7 (17.2)	67.4 ± 38.4 (42.9)	46.4 ± 32.0 (20.8)	63	5.2 ± 1.8 (4.2)	3.7 ± 0.3 (3.8)	534	344
Estimated[c]									
All data	1396	8.9 ± 35.7 (2.8)	–	–	–	–	–	–	–

[a]Also shown are subsets of samples predominantly influenced by aerosol source as determined in section 2.4. Estimated data based on historical aerosol data and scavenging ratios are included.
[b]To obtain more representative ratios, data were excluded with TSP/SRP <7 n*M* and DIN/TSN values <1 μ*M*.
[c]Wet deposition concentrations were estimated based on equation (4) and average historical dust and DIN aerosol concentrations.

dust-dominated rain samples. In addition to lower SRP inputs, Miami rain also yielded higher DOP inputs. In Miami, the median DOP concentration ~32 n*M* was 3 times higher than the median DOP concentration in Barbados (11 n*M*). Larger concentrations of DOP in Miami may indicate that the terrestrial (i.e., continental North American) sources of DOP have a greater impact than the marine sources. This hypothesis is supported by a correlation between DOP and NO_3^- and DOC (both with an $r^2 = 0.61$) in the absence of biomass burning samples (Table 6). Excluding biomass burning, terrestrial anthropogenic pollution is the main source of NO_3^- and water-soluble organic carbon [*Zamora et al*., 2011].

[36] Despite relatively small number of samples for categories other than dust and pollution, our data nonetheless suggest that soluble P concentrations could be linked to source types. On the basis of the data presented in Table 5, rain events that occurred during dust days generally had higher levels of SRP than during pollution or sea spray days. Relatively high SRP concentrations in rain dust samples are consistent with the observed relationship between dust and SRP concentrations in aerosols. However, we saw no clear associations between the concentrations of SRP and DOP and the amount of dust collected on the rain filter in Miami rain ("ash" in Table 6, which is defined as the particle mass after ashing the filter at 500 °C normalized to the volume of rain that was filtered). There was also no relationship to other dust tracers (Mn and Al) (Table 6), nor was there a direct relationship between soluble P concentrations in rain with sea salt or variables indicative of pollution (nss-SO_4^{2-} and the V/Ti ratio) in Miami. Although some rain samples had basic pH values up to 8.8, indicating some neutralization of acids, possibly from dust-based $CaCO_3$ [*Nenes et al*., 2011], no relationship was observed between pH and SRP or dust. These findings are in contrast to several studies that found good correlations (in aerosols) between SRP and nss-SO_4^{2-} and -Ca^{2+} in east China [*Chen and Chen*, 2008] and between SRP and nss-Ca^{2+} in the Bay of Bengal [*Srinivas and Sarin*, 2012]. A lack of strong correlations with different source indicators in rain indicates that there was no predominant source of SRP in Miami or that rain P sources are relatively complex compared with those in eastern China, where anthropogenic aerosol concentrations are in general very high and intense pollution events very frequent.

[37] *Migon and Sandroni* [1999] suggested that SRP concentrations would be expected to be partially pH dependent in Saharan dust samples because of the adsorption of soluble P onto iron oxides between pH of 5 and 8. However, there was no significant correlation between H^+ concentrations and SRP or DOP in dust rain samples ($r^2 = 0.12$ and $r^2 = 0.04$ [$p = 0.41$ and $p = 0.64$] for SRP and DOP, respectively). The lack of a strong relationship between soluble P concentrations and H^+ concentrations in dusty rain suggests that acidity is not the primary cause for the higher P solubility of pollution-dominated aerosol samples.

3.3. Deposition of P and atmospheric N*

[38] The aims of this section are twofold. First, we use the information presented in sections 3.1 and 3.2 to estimate the magnitude of historical dust-derived TP and SRP deposition at Barbados and Miami. Then, based on these estimates, we link historical P deposition to historical N deposition and

Table 6. Binary Correlation Coefficient for Miami Rain SRP and DOP Data[a]

	SRP	DOP	DOC	NO_3^-	NH_4^+	DON	Sea salt	Cl^-	nss-SO_4^{2-}	K^+	Ca^{2+}	Al	V/Ti ratio	Mn	Ash	Ni	Cu
SRP	–	−0.22	0.19	0.13	0.16	0.07	0.00	0.00	0.02	0.17	0.00	0.00	0.01	0.05	0.15	0.01	0.01
SRP (non–"BB" samples)	–	−0.01	0.07	0.22	0.15	0.08	−0.03	−0.01	0.02	0.07	0.12	−0.02	−0.03	0.07	0.21	−0.03	−0.04
DOP	−0.22	–	0.14	**0.35**	0.04	0.12	0.01	0.01	0.00	0.07	0.01	0.04	0.02	0.01	0.00	0.03	0.03
DOP (non–BB samples)	−0.01	–	**0.61**	**0.61**	0.13	0.23	−0.02	0.03	0.20	−0.03	−0.02	0.13	−0.04	−0.02	−0.08	−0.03	−0.04

[a]Bold entries represent $p < 0.05$ correlations with r^2 values >0.3. BB = biomass burning.

provide estimates of seasonal and interannual variability in N/P ratios in deposition.

3.3.1. Historical aerosol P estimates

[39] To determine the historic dry deposition of P, we first must estimate historic aerosol P values. In section 3.1, we showed that nearly all variabilities in aerosol TP concentrations were caused by dust. Thus, we use a method similar to previous authors [*Mahowald et al*., 2008; *Prospero et al*., 1996], where TP is approximated from the dust-TP relationship presented in Figure 2 and from dust records (available in Barbados from 1973 to 2001 and in Miami from 1998 to 2008).

[40] On the basis of these dust-derived TP estimates, there is a clear seasonal trend in expected TP concentrations in Barbados and Miami (Figure 5); the highest estimated TP concentrations in Barbados and Miami occur between June and September. On the basis of the dust-TP relationship and historical dust concentrations, median dust-derived aerosol TP concentrations in Barbados and Miami in June-September are estimated at 409 and 181 pmol TP m^{-3}, respectively (Figure 5). In October to May, median concentrations at both sites are 3–5 times smaller, at 90 and 59 pmol TP m^{-3} in Barbados and Miami, respectively. The variability associated with the estimated aerosol TP concentrations is quite large (see Figure 5) and is indicative of the variety of factors that affect dust concentrations, which include climate in Africa [*Prospero and Lamb*, 2003], large-scale meteorological phenomenon such as the North Atlantic Oscillation, and local meteorological conditions [*Moulin et al*., 1997]. *Prospero et al*. [1996] also expect high seasonal variability in dust (and thus TP) deposition to the North Atlantic Ocean. They indicated that dust-derived TP concentrations should change orders of magnitude over periods of time ranging from days to weeks and in annual means by a factor of 3 over decades in response to climate factors [*Prospero and Lamb*, 2003].

[41] Note that by estimating aerosol TP concentrations from dust alone, we cannot account for pollution-derived TP in Miami (no confirmed pollution days were observed in Barbados). In Miami, we derive a low-end estimate of the pollution-derived inputs based on the number of days determined as pollution dominated during May 2007-May 2009 (~20% of all days) and the average amount of TP (0.137 ± 0.136 nmol m^{-3}) observed on pollution days that is in excess to that expected based on dust concentrations. From these values, we make a very rough estimate that pollution-derived TP in Miami accounts for at least 9% of annual TP deposition. It is likely that the actual contribution is larger because our criteria exclude days with mixed sources that include pollution and because the chemical data used in source categorization were not available for all days. For comparison, *Mahowald et al*. [2008] estimated that globally ~17% of TP is from non–dust sources.

[42] In addition to dust-derived aerosol TP estimates, we can also estimate historical dust-derived aerosol SRP from Barbados dust samples (Figure 4a). SRP is estimated to contribute 8% of dust TP (section 3.1.2). A solubility of 8% compares well with literature estimates for soluble P from dust (Table 7). It is slightly lower than the range of the estimated 15%–30% bioavailability of Saharan dust samples from *Anderson et al*. [2010] and model estimates of 14.7% for the North Atlantic [*Mahowald et al*., 2008]. Note, however, that solubility can vary somewhat based on dust

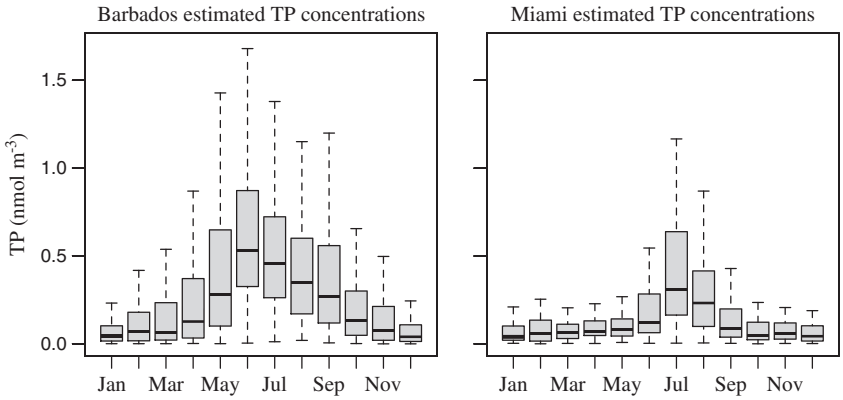

Figure 5. Monthly estimated concentrations of dust-derived TP in Barbados and Miami based on an average of 880 ppm TP from dust and a time series of dust concentrations at both stations (Barbados: 1973–2001 and 2007–2008, Miami: 1998–2003 and 2007–2009). A clear seasonal cycle in TP deposition at both stations is expected based on these data. Note that in order to better illustrate the seasonal cycle, outliers are not shown in the figures. Also note that these estimates do not include TP from pollution sources.

Table 7. Literature Estimates of SRP Solubility From TP in Dust Aerosols

SRP/TP (%)	Sample type	Reference
8% ± 3%	Saharan dust (Barbados)	This study
18% ± 11%	Saharan dust (Miami)	This study
8%	Saharan dust	*Lepple* [1975]
11%	Loess	*Herut et al*. [1999]
25%	Saharan dust	*Carbo et al*. [2005]
16% ± 10%	Saharan dust	*Chen and Chen* [2008]
8%–10%	Saharan dust	*Herut et al*. [2002]
10%–15%	Saharan soil	*Ridame and Guieu* [2002]
8%–100%	Mixed Mediterranean samples (including some Saharan dust)	*Bergametti et al*. [1992]

concentrations in the extractant [*Ridame and Guieu*, 2002]. Using a constant SRP/TP fraction for all samples, we estimate the average dust-derived aerosol SRP concentrations at 27 ± 36 and 23 ± 94 pmol TP m^{-3} in Barbados and Miami, respectively.

3.3.2. P and N dry deposition

[43] In addition to dust, the historical aerosol record at Miami and Barbados includes DIN (ammonium + nitrate). DIN records began in 1989 in Barbados and 1998 in Miami. Because historical DIN measurements are available, estimated historical phosphorus deposition can be placed in context with the inorganic N that was codeposited. Note that because it does not take into account non–dust sources of SRP, our dust-derived SRP estimate is a lower-end estimate of actual SRP deposition. Therefore, we also provide an upper-end estimate of SRP deposition by assuming that all TPs are in the form of SRP. In this way, we obtain a range of possible SRP values, with which we can calculate a range of possible historical aerosol inorganic N/P deposition ratios at the sites.

[44] We estimate the dry deposition flux (F_{dry}) of aerosol inorganic P and N using the following formula:

$$F_{dry} = CV_d \quad (1)$$

where C is the atmospheric SRP concentration (in nmol m^{-3}) and V_d is the velocity ($m\,s^{-1}$) for dry deposition. The deposition velocity of aerosol P was estimated at 0.01 m $s^{-1} \pm$ a factor of 3 [*Duce et al*., 1991], as was that of NO_3^-, because it was found primarily in the coarse size fraction [*Zamora et al*., 2011]. As in *Spokes et al*. [2000], we estimated ammonium deposition velocity at 0.006 m $s^{-1} \pm$ a factor of 3 [*Spokes et al*., 2000].

[45] It is important to note that the removal of aerosols from the atmosphere is still very poorly understood. V_d is likely to be impacted not only by aerosol size and hygroscopicity but also by meteorological parameters such as rainfall, relative humidity, and wind speed [*Prospero and Arimoto*, 2009]. Thus, V_d estimates are likely to have large associated errors, which are commonly assumed to be on the order of a factor of 3 based on various size-dependent processes [*Duce et al*., 1991]. Dry deposition estimates are presented in Table 8. Owing to the high levels of uncertainty in V_d, these estimates include the range of average dry deposition estimates based on a factor of 3 errors in V_d. However, because V_d errors increase at high wind speeds, an even larger error estimate might be more realistic in some circumstances [*Prospero and Arimoto*, 2009]. As a single V_d value cannot account for seasonal and spatial variability, interpretations of wet nutrient deposition (section 3.3.3) are much more straightforward than of dry deposition.

[46] On the basis of the estimated daily dry deposition presented in Table 8, both Barbados and Miami have similar average P inputs from dry deposition (in Barbados and Miami, respectively; dust-derived SRP deposition = 0.022 and 0.019 μmol m^{-2} d^{-1} and TP deposition = 0.284 and 0.250 μmol m^{-2} d^{-1}). For comparison, previous measurements in the area from cruise data gave a SRP flux of 0.009 μmol m^{-2} d^{-1} [*Baker et al*., 2010].

[47] Estimated inorganic N/P ratios were an order of magnitude different depending on whether TP or SRP was used to approximate inorganic P deposition (Figure 6). As with dust, N/P ratios vary strongly with season; winter N/P ratios (November-March) were more than half of the ratios in April-October because of the higher inputs of dust and P during the summer (Figure 6). Estimated N/P ratios in deposition were also highly interannually variable; for example, median inorganic N/P ratios during nonsummer periods in

Table 8. Estimated Wet and Dry Deposition of Nutrients in Barbados and Miami (μmol P or N m^{-2} d^{-1})[a]

	Annual rainfall[b] (cm yr^{-1})	Wet SRP flux	Wet DOP flux	Wet DIN flux	Wet DON flux
Barbados					
Observed	118	0.19 ± 0.12	0.06 ± 0.03	23.0 ± 12.6	2.6 ± 3.6
Estimated[c]	118	0.15 ± 0.20	n.a.	17.5 ± 29.1	n.a.
Miami					
Observed	149	0.11 ± 0.10	0.15 ± 0.09	69.4 ± 40.4	5.3 ± 6.5
Estimated[c]	149	0.04 ± 0.15	n.a.	n.a.	n.a.

	Dry SRP flux		Dry TP flux		Dry DIN flux		Dry WSON flux[d]	
	av.	Sensitivity range	av.	Sensitivity range	Av.	Sensitivity range	Av.	Sensitivity range
Barbados								
Dust	0.10 ± 0.03	0.03–0.31	0.56 ± 0.23	0.19–1.70	14.8 ± 6.5	5–44	2.3 ± 2.0	0.8–6.9
Sea spray	0.05 ± 0.04	0.02–0.16	0.09 ± 0.07	0.03–0.28	8.0 ± 2.8	2–24	1.4 ± 0.5	0.5–4.2
Biomass burning	0.05 ± 0.01	0.02–0.14	0.08 ± 0.08	0.03–0.24	19.0 ± 16.3	6–57	3.8 ± 2.0	1.3–11.5
All data[e]	0.02 ± 0.03	0.01–0.07	0.28 ± 0.38	0.09–0.85	11.3 ± 8.3	4–34	2.2 ± 1.9	0.7–6.7
Miami								
Dust	0.10 ± 0.08	0.03–0.31	0.56 ± 0.21	0.19–1.68	37.9 ± 11.3	13–114	5.1 ± 2.6	1.7–15.2
Biomass burning	0.11 ± 0.04	0.04–0.33	0.20 ± 0.13	0.07–0.59	51.0 ± 35.9	17–153	4.4 ± 3.7	1.5–13.1
Pollution	0.06 ± 0.07	0.02–0.18	0.16 ± 0.13	0.05–0.48	30.7 ± 18.3	10–92	4.5 ± 2.7	1.5–13.5
All data[e]	0.02 ± 0.07	0.01–0.06	0.25 ± 0.95	0.08–0.75	65.5 ± 119.3	22–196	4.9 ± 5.1	1.6–14.6

[a]The "sensitivity range" for dry deposition is calculated based on the average dry deposition flux and a factor of 3 uncertainty in deposition velocity.
[b]Average yearly rainfall from M.D. Winsburg (Precipitation data: Miami, 2009, Florida Climate Center, http://coaps.fsu.edu/climate_center/data/precip_-miami.shtml) and *Rouse* [1962].
[c]Estimated based on equation (4) and average historical dust and DIN aerosol concentrations.
[d]Dry WSON flux is from *Zamora et al*. [2011] and includes volatile basic organic N flux.
[e]SRP and TP values are estimated for these samples based on dust concentrations (see section 3.3.2).

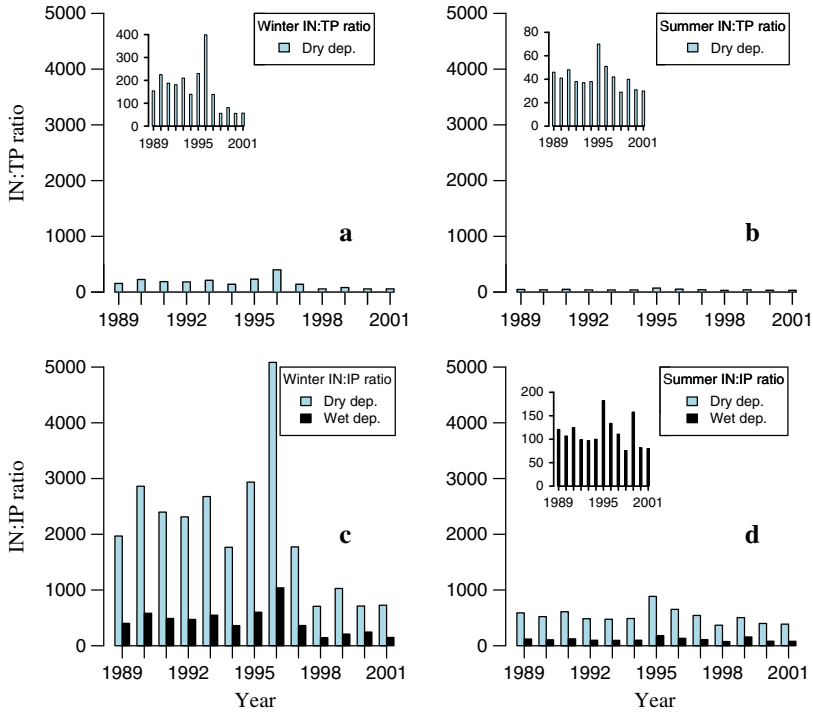

Figure 6. Estimated median seasonal N/P deposition ratios in Barbados with insets to show detail. Dry deposition (light blue fill) and wet deposition (black fill) N/P ratios are separated. Winter is defined as November to March, and summer is defined as April to October. N/P deposition ratios are estimated from measured aerosol DIN values and estimated aerosol P values based on dust concentrations. The lower estimate for N/P ratios in deposition is determined from the DIN/TP ratio (a and b), and the upper estimate of N/P deposition ratios is determined from the DIN/SRP ratio (c and d). Wet deposition ratios are estimated based on scavenging ratios and aerosol concentrations. As TP was not measured for wet deposition, only DIN/SRP ratios for wet deposition are shown (c and d).

Barbados were 4 times higher in 1996 than in 2001 (Figure 6). The range of estimated dry deposition inorganic N/P ratios in Barbados throughout the year (~500–5000) incorporates but exceeds the range of previously measured N/P ratios (870:1000) in the region (*Baker et al.* [2010], from their region 1e), in part, because of the longer time period over which samples were gathered.

[48] To put N/P ratios in atmospheric deposition in context of their potential impact on ocean surface water nutrient balance, we compared N/P ratios in deposition to the canonical seawater Redfield molar ratio of 16 N/1P. N in excess of that expected from Redfield values is defined as follows:

$$\text{Excess } N = \text{DIN} - 16\ \text{SRP}, \tag{2}$$

where DIN is the sum of $NO_3^- + NH_4^+$.

[49] The dry deposition rates of excess N are presented in Figure 7. Median annual inorganic excess N deposition to Barbados is between 7 and 11 μmol N m^{-2} d^{-1}, depending on whether upper or lower estimates of P deposition were used (i.e., SRP or TP). The inorganic excess N deposition estimate agrees exactly with a previous estimate for the region (7 μmol N m^{-2} d^{-1}) from *Baker et al.* [2010] (based on their region 1e). In Miami, annual dry inorganic excess N deposition is between 62 and 65 μmol N m^{-2} d^{-1}. Despite highly variable N/P ratios, Figure 7 indicates that the high- and low-end estimates of excess N deposition were relatively similar within sites because N deposition is often very much larger than P deposition. Even the sevenfold differences in N/P ratios in deposition between 1996 and 1998 in Barbados led to a maximum estimated difference of only 0.8–1.9 μmol N m^{-2} d^{-1} of excess N deposition between the two periods.

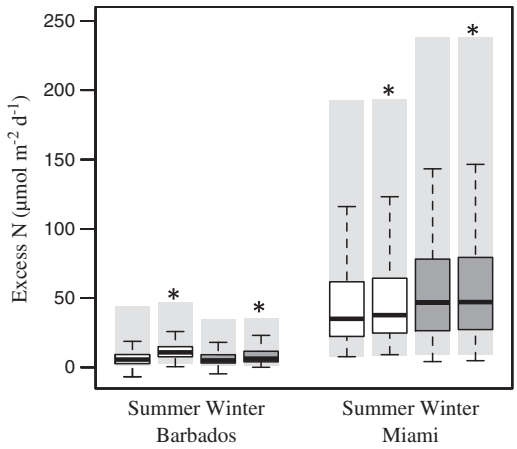

Figure 7. Upper and lower ranges of estimated excess inorganic N in estimated dry deposition at Barbados (1989–2001) and Miami (1998–2003). Seasonal ranges are separated, with white box plots for the summer (April-October) and dark gray box plots for the winter (November-March). Two estimates are shown for each season, an upper estimate and a lower estimate. The upper range for excess inorganic N deposition (indicated by an asterisk symbol) is derived from using P = SRP for N/P ratios; the lower range is derived from using P = TP for N/P ratios. Box plots show the median in bold, the 25th and 75th percentiles of the concentrations (box), and the range of the data excluding outliers as whiskers (outliers, values that exceed 150% of the interquartile range, are not shown). The shaded areas indicate the lower and upper quantile values expected, given a factor of 3 error in assumed deposition velocities. Note that in Barbados, negative excess N deposition values sometime occur—negative values should be interpreted as excess phosphorus deposition rather than excess N deposition.

[50] It is interesting to note that with increasing dust concentrations, some of the dry deposition estimates in Barbados have a negative excess N signal (Figure 8). This result indicates excess P instead of excess N (i.e., P exceeds Redfield expectations), and its significance is that on dusty days, deposition may sometimes add more biologically available P to the ocean than deposited N demands, actually reducing P stress. However, high "excess P" in dry deposition was only observed in the upper-end estimates of inorganic P inputs (i.e., where P = TP) and may not be environmentally relevant, since not all of this P is likely to be bioavailable. In most cases in Barbados and in all cases in Miami, deposition was a net source of excess N to surface waters, a result that fits well with model expectations [*Okin et al.*, 2011].

[51] A caveat with the estimated excess N dry deposition data is that while water-soluble organic P is included in the TP measurements, water-soluble organic N (WSON) is not taken into account. *Zamora et al.* [2011] indicate that dry WSON deposition is ~1.3–2.2 μmol m^{-2} d^{-1} in Barbados and ~2.5–5.0 μmol m^{-2} d^{-1} in Miami (not including a factor of 3 uncertainty because of poorly constrained V_d for WSON). Other estimates in the North Atlantic indicate that WSON inputs at other locations may be higher [*Lesworth et al.*, 2010]. Therefore, including WSON may increase excess N deposition estimates by at least an additional 16% and 8% in Barbados and Miami, respectively. Incorporating WSON into the N/P ratios and assuming a WSON dry deposition velocity of 0.012 m s^{-1} [*Spokes et al.*, 2000], we estimate that ~9–13 μmol N m^{-2} d^{-1} in excess of Redfield ratios to the ocean surface is deposited in dry deposition near Barbados, and ~66–70 μmol N m^{-2} d^{-1} in excess of Redfield ratios is deposited in Miami.

3.3.3. P and N wet deposition

[52] *Prospero et al.* [2010] estimated that wet deposition is the dominant source of dust in the western subtropical North Atlantic (in Florida accounting for 70%–80% of total dust deposition); *Baker et al.* [2010] also indicated that wet deposition is dominant in the broader North Atlantic region. Thus, we supplement the dry deposition estimates provided above with wet deposition estimates of N and P in deposition.

[53] Rainfall nutrient deposition is expected to be highly variable, as both aerosol nutrient concentrations and rainfall fluctuate in space and time. Thus, we employ two complementary methods to better understand the magnitudes and variability of P and N wet deposition. First, concentrations of measured nutrients in wet deposition during the 2007 and 2008 field campaigns in Barbados and between 2007 and 2009 in Miami were gathered and compared to average annual rainfall at each site. The flux of wet deposition (F_{wet}) was determined from

$$F_{\text{wet}} = C_p R \tag{3}$$

where C_p is the concentration (μmol L^{-1}) of nutrients in precipitation and R represents event rainfall (in mm).

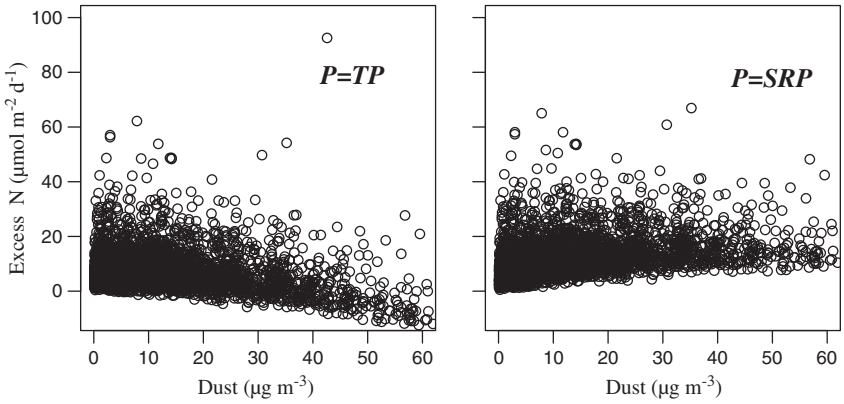

Figure 8. Excess N in Barbados dry deposition (μmol N m^{-2} d^{-1}) calculated when P is estimated from (a) TP and (b) SRP in 1989 to 2001. Although the graphs contain most of the data, for purposes of visualizing trends, some extreme data are not included.

[54] Wet deposition measurements in Barbados cover a relatively brief span of time (~10 weeks) in this study. Thus, a second, complementary method using scavenging ratios collected during the 2007 and 2008 field campaigns and historical aerosol measurements is employed to better understand the historical magnitudes and variability of P and N wet deposition. Scavenging ratios (SR) in Barbados are determined by

$$\mathrm{SR} = C_p / C_a \tag{4}$$

where C_a is the concentration of aerosols over a period of time (in nmol m^{-3}) and C_p is the volume weighted mean concentration in rain (nmol kg^{-1} water) over the same period of time. Scavenging ratios are presented in Table 9.

[55] Because aerosols were only gathered when winds blew from a marine sector but wet deposition was sampled independently of wind sector, precipitation and aerosol samples concurrently collected did not always sample the same air masses. In Barbados, this effect is minimal because winds blow from the east nearly 95% of the time. The Miami winds were out of sector more often, however. Thus, measured scavenging ratios were not accurate. Instead, the dust scavenging ratio of 200 nmol kg^{-1} water per nmol m^{-3} air from *Duce et al*. [1991] was used for phosphorus. This ratio was based on measurements of dust in aerosols and rain over the North Atlantic. For comparison, a dust scavenging ratio of 241 nmol kg^{-1} water per nmol m^{-3} air for June-September was calculated here from sampling stations in South Florida (based on data presented in *Prospero et al*. [2010]) and dust aerosol measurements at our coastal Miami site; the values from Florida appear to agree relatively well with the estimate of *Duce et al*. (1991).

Table 9. Scavenging Ratios in Miami and Barbados

	Barbados	Miami
SRP	835	200[a]
$NO_3^- + NO_2^-$	363	–
NH_4^+	221	–
WSON	86–175	–

[a]Estimated from the North Atlantic dust scavenging ratio of 200 [*Duce et al*., 1991].

[56] Measured and estimated historical wet deposition in Barbados and Miami is shown in Table 8. Measured wet deposition contributed 0.25 and 0.29 μmol TSP m^{-2} d^{-1} from both DOP and SRP in Barbados and Miami, respectively, during our sampling periods. Rainfall is 25% higher in Miami than in Barbados, which is one likely reason why TSP flux from wet deposition was similar at both sites despite lower dust concentrations in Miami. Also, Miami is much more impacted by polluted (i.e., North American) air masses than Barbados (although pollution only contributes to the observed TSP flux and not the dust-estimated flux shown in Table 8).

[57] Interestingly, measured inputs of DOP were twice as high in Miami as in Barbados, doubling the deposition of measured TSP. DOP measured in rain and aerosols at other sites was a similarly large contributor to TSP concentrations (see Table 10; also [*Chen et al*. 1985, 2006, 2007] and [*Graham et al*. 1979]). Our ability to compare measured wet deposition in Miami and Barbados is limited to some extent because Barbados rain was only gathered in the summer, when dust inputs are typically high and biomass burning inputs tend to be relatively low. However, when scavenging ratios are used to approximate inorganic N and P deposition in Barbados using the long-term dust record, we find slight decreases in the concentrations of P (owing to less dust year-round than in the summer when the sampling period took place), slightly higher N inputs (because of relatively higher N species concentrations in seasons other than summer), and much larger variability in the data (owing to the longer periods of time aerosols were sampled).

[58] Although P wet deposition levels were similar at both sites during the sampling periods, measured N/P ratios in rain were different (Table 5). Both sites yielded ratios with positive excess N, similar to numerous observations in other locations (Table 10). However, Miami yielded higher N/P wet deposition ratios than Barbados because of higher N concentrations associated with the more frequent impact of terrestrial/polluted air masses. Higher N/P ratios in polluted areas have been previously predicted and observed [*Chen and Chen*, 2008; *Mahowald et al*., 2008].

[59] Interestingly, measured NO_3^- and NH_4^+ ("DIN")/SRP ratios were higher than measured TSN/TSP ratios, and by inference, the dissolved organic N (DON)/DOP ratios are

Table 10. Literature Estimates of Wet Deposition Fluxes ($\mu mol\ m^{-2}\ d^{-1}$)[a]

Location	n	$NO_3^- + NO_2^-$	NH_4^+	DON	SRP	DOP	%DOP	Inorganic N/P	Reference
Mixed									
Barbados	21	13.3 ± 6.1	9.7 ± 6.5	2.6 ± 3.6	0.070 ± 0.043	0.021 ± 0.012	23%	329	This study
Miami	67	41.6 ± 22.0	29.8 ± 20.8	6.1 ± 7.3	0.050 ± 0.046	0.056 ± 0.034	53%	1428	This study
Six NADP sites in Florida	149	18 ± 2	8 ± 1	–	0.036 ± 0.008	<0.005	<13%	733	*Grimshaw and Dolske* [2002]
Barbados	1	6	3	–	0.604	–	–	16	*Talbot et al.* [1986]
Greece	41	25	29	–	0.187	–	–	288	*Markaki et al.* [2003]
Yellow Sea	198	69	96	–	1.404	–	–	118	*Zhang et al.* [2008]
East China Sea	75	58	88	–	0.176	–	–	830	*Zhang et al.* [2008]
Erdemli, Turkey	61	38	–	–	0.726	–	–	>49	*Özsoy* [2003]
New Zealand	7	–	–	–	0.265	0.539	67%	–	*Chen et al.* [1985]
Amazonia	210	32	22	–	0.066	0.482	88%	818	*Williams et al.* [1997]
New Jersey	4	148	143	109	0.2	–	–	1455	*Altieri et al.* [2009]
Dust									
France	25	–	–	–	0.324	0.159	33%	–	*Migon and Sandroni* [1999]
Erdemli, Turkey	9	55	–	–	0.665	–	–	>83	*Özsoy* [2003]

[a]Wet deposition fluxes are calculated from precipitation rates [*Adler et al.*, 2003] and rain nutrient concentrations.

smaller than the DIN/SRP ratios. On the basis of equation (4), the inclusion of the organic P fraction in deposition in Miami and Barbados reduces the estimated excess N entering the surface ocean from the atmosphere. Even so, the TSN/TSP molar ratios in wet deposition are still much greater than the canonical Redfield ratio 16:1 (Table 5). If the DON and DOP in deposition were biologically available, it would spur new production to values higher than expected based solely on inorganic N and P deposition values.

4. Summary and Conclusions

[60] Here we characterize the levels and seasonal and interannual variability of TP, SRP, N/P ratios, and excess N in atmospheric deposition to the western subtropical North Atlantic. As expected, there was a strong correlation between TP and dust at our sites, equaling ~880 ppm. There is also a pollution source of TP observed at the Miami site that adds at minimum an additional 9% to the TP deposition at that site. Similarly to TP, SRP has a substantial dust source. However, in Miami, nondust inputs of SRP (such as those from sea spray and combustion sources) are believed to contribute a considerable portion of SRP because of the greater solubility. We do not attempt to measure the annual contribution of pollution-derived SRP to the deposition fluxes, in part, because a background level of sea spray–derived SRP makes it difficult to interpret net SRP concentrations from combustion sources. Nonetheless, pollution-derived SRP likely contributes more than the 9% expected in TP because soluble P is higher in pollution aerosols than in dust aerosols.

[61] Interestingly, in addition to providing nonnegligible levels of SRP, pollution also appears to be the main source of DOP, which, on average, contributes 28%–44% of the total soluble P pool measured in Miami and Barbados. Because DOP in wet deposition is likely to be largely bioavailable, it may be a major source of new, nonrecycled P to this ocean region. Dust does not appear to be a large source of DOP. When organic N and P are incorporated into estimates of N/P deposition, N/P ratios in wet deposition become smaller; therefore, previous assessments may have slightly overestimated excess N deposition to the ocean surface and its biological impacts by not including the organic fraction of deposition.

[62] On the basis of the strong correlation between TP and dust, we find that P dry deposition was highly variable, with 2–10 times more P deposited in the summer than during other periods of the year. In the subtropical western North Atlantic, the strong seasonal cycle in P flux results in a large variation in the N/P ratios in deposition, with up to an eightfold difference in the interannual seasonal ratios and lower ratios during the summer months. The seasonal variation in P deposition may have important biological implications; for example, via the stimulation of N_2 fixation [*Mills et al.*, 2004], although further biological studies are needed to more fully assess the bioavailability of atmospheric-derived P.

[63] Despite the inputs from soluble organic matter and high seasonal variability of P inputs, inorganic excess N deposition rates were always positive at Barbados and Miami because of the large N inputs in the region. This relationship held true even given the large uncertainties in dry deposition velocity. On the basis of the Barbados measurements, atmospheric wet deposition in the western subtropical North Atlantic yields 16–22 μmol excess $N\ m^{-2}\ d^{-1}$, including the

organic fraction. Atmospheric dry deposition (including organic deposition) accounts for 9 to 13 μmol N m^{-2} d^{-1} in excess of Redfield ratios to the ocean surface. When we take into account the uncertainties in the dry deposition velocity, the range is 3–40 μmol N m^{-2} d^{-1}. On the basis of the Miami data, in the northwestern portion of the subtropical North Atlantic, wet deposition contributed 71–72 μmol N m^{-2} d^{-1} in excess of Redfield ratios, and dry deposition contributed another 66–70 μmol N m^{-2} d^{-1} (22–210 μmol N m^{-2} d^{-1}, taking into account uncertainties in deposition velocity). Clearly, dry deposition is by far the most poorly characterized component in estimating deposition.

[64] Overall, we find that even though anthropogenic pollution is creating more soluble inorganic and organic phosphorus, atmospheric deposition is consistently a source of excess N, even during large dust events. This finding holds true despite the nonnegligible sea spray source of P, which future studies should account for in order to avoid overestimating new atmospheric SRP deposition to the ocean. This result indicates that the amount of P stress in the surface waters of the Atlantic is likely to continue to increase because of atmospheric nutrient deposition.

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